

High-Resolution Soft X-ray Emission and Absorption Spectra of Amorphous Carbon Films

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INTRODUCTION

Amorphous carbon films are important and interesting materials for both industrial applications and materials science. It is thought that they consist of a random structure of sp^2 - and sp^3 -configured carbon atoms, and that the structure and chemical bonding states determine their mechanical and optical properties. Thus, characterization studies of amorphous carbon films to clarify the structure and chemical bonding states have been conducted by many researchers using various analytical methods such as Raman spectroscopy, x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and electron energy loss spectroscopy (EELS). Recently, near-edge x-ray absorption spectroscopy using highly brilliant synchrotron radiation has been utilized to characterize amorphous carbon films [1, 2], and this proved able to obtain electronic-structure information about unoccupied orbitals, which directly reflect chemical bonding states, from the x-ray absorption spectra at the C K threshold. However, the fine structure observed in the absorption spectra has not been clearly assigned yet. In addition, few studies of soft x-ray emission spectroscopy, which provides electronic-structure information about occupied valence orbitals, have been performed for characterizing amorphous carbon films [3].

We have therefore measured the high-resolution soft x-ray emission and absorption spectra of amorphous carbon films to characterize the films from the electronic-structure information of both occupied and unoccupied orbitals, and to evaluate the feasibility of using soft x-ray spectroscopy for characterizing amorphous carbon. In this paper, we describe the high-resolution C K x-ray emission and absorption spectra of amorphous carbon films deposited by various deposition methods and conditions.

EXPERIMENT

Amorphous carbon films were deposited by RF, ion-beam, and electron-cyclotron-resonance (ECR) sputtering, under various deposition conditions. For the RF-sputtered carbon films, the pressure of the source gas was 5×10^{-2} (denoted by R1 in Fig. 1), 1×10^{-1} (R2), or 1×10^{-2} Torr (R3). For the ion-beam-sputtered carbon films, the annealing temperature was as-dep. (I1), 400°C (I2), or 700°C (I3). For the ECR-sputtered carbon films, the acceleration voltage was -20 (E1), -75 (E2), or -100 V (E3). The thicknesses of the RF- and ECR-sputtered carbon films were approximately 40 nm, and that of the ion-beam-sputtered carbon was 30 nm.

Spectroscopic measurements of x-ray emission and absorption in the C K region were made at the Advanced Light Source (ALS). X-ray emission spectra were measured using a grating x-ray spectrometer installed in beamline (BL) 8.0 [4]. The resolving power ($E/\Delta E$) of the spectrometer was estimated to be more than 500 in the C K region, using a 50- μ m entrance slit and a 600-lines/mm spherical grating which had a 10-m radius. The total-electron-yield (TEY) absorp-

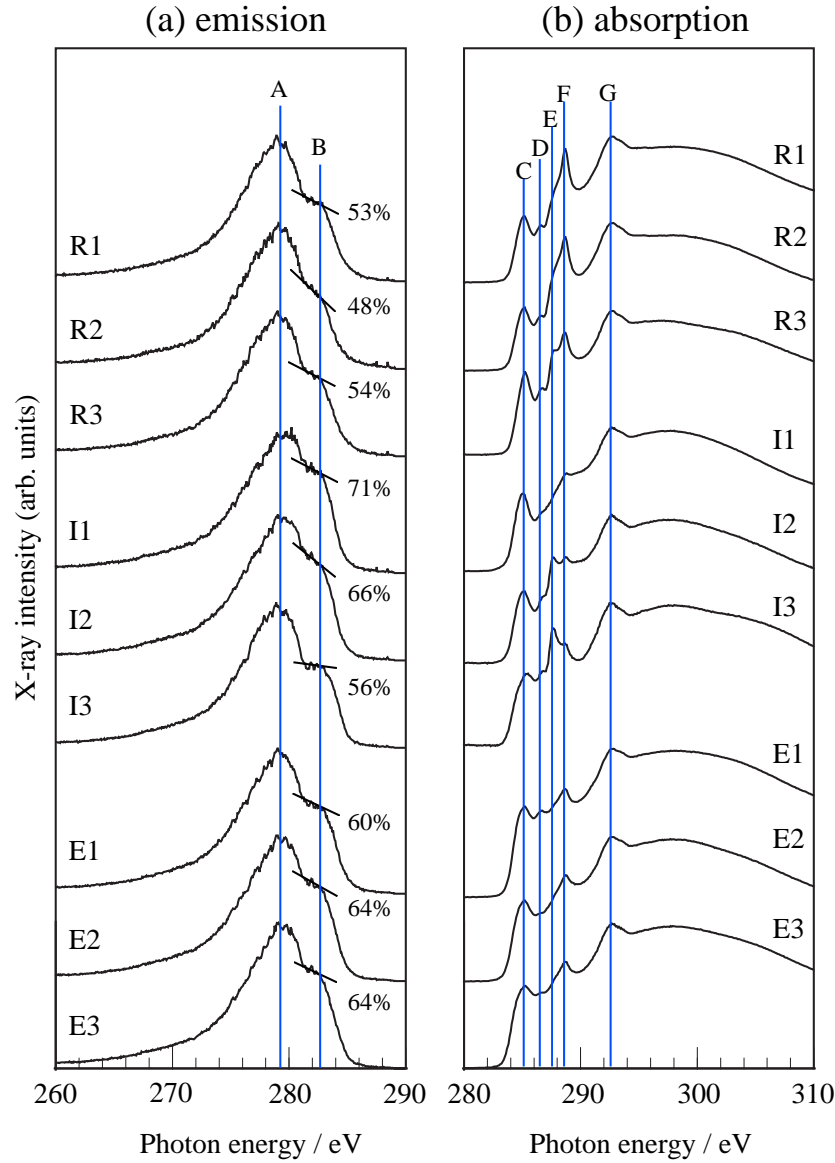


Figure 1 Left panel (a) shows the C K x-ray emission spectra of amorphous carbon films deposited by RF sputtering (denoted by R1–3), ion-beam sputtering (I1–3), and ECR sputtering (E1–3), each for three different deposition conditions. The excitation energy for the x-ray emission measurements was tuned to 320 eV. Specific spectral features in the amorphous carbon films are denoted by A and B. Right panel (b) shows the CK x-ray absorption spectra of amorphous carbon films deposited by RF sputtering (R1–3), ion-beam sputtering (I1–3), and ECR sputtering (E1–3), each for three different deposition conditions. Specific spectral features in the amorphous carbon films are denoted by C–G.

tion spectra were measured by monitoring the sample photocurrent in BL-6.3.2 [5]. The resolving power of the TEY-absorption measurements was estimated to be about 1600 using a 600-lines/mm variable-line-spacing grating and a 20- μ m exit slit. In these TEY absorption measurements, a photodiode detector which had negligible carbon contamination was used as an incident-beam-intensity monitor to eliminate the effect of carbon contamination on the beamline optics.

RESULTS AND DISCUSSION

Figure 1 shows (a) x-ray emission spectra and (b) TEY absorption spectra in the C K region of the amorphous carbon films deposited by the above-mentioned deposition methods and conditions (R1-3, I1-3, and E1-3). In the emission spectra, the spectral features of the amorphous carbon films were essentially similar, consisting of a broad main peak around 279 eV (denoted by A in Fig. 1) and a high-energy shoulder peak near 283 eV (B). However, the peak-height ratio of the shoulder-peak to the main-peak depended on the deposition method/conditions: it ranged from 48% to 71% among these films. These spectral features therefore suggest that local structures and chemical bonding states are essentially similar among the amorphous carbon films, but that their ratio, for example of sp^2 - and sp^3 -configured carbon atoms, differs depending on the deposition method/conditions.

In the absorption spectra, a fine structure consisting of five peaks, observed at 285 eV (C in Fig. 1), 286.5 eV (D), 287.5 eV (E), 288.5 eV (F), and 292.5 eV (G), was clearly seen among these films at the C K threshold. This fine structure has not been measured by conventional EELS [6] because this method has lower energy resolution than soft x-ray absorption spectroscopy using synchrotron radiation. Although the relative peak intensities among these five peaks depended on the deposition method/conditions, the five peaks were observed at constant energy positions. This also suggests that common local-structures/chemical-bonding-states exist in the amorphous carbon films, but that their ratios differ among the films. Spectral analysis using DV (discrete variational) $X\alpha$ molecular orbital calculations is now in progress.

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